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A MICRO-CALORIMETER FOR MEASUREMENT OF SMALL HEAT CHANGES

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ABSTRACT. A calorimeter has been designed to study the heats of mixing of binary liquid systems. The accuracy of the calorimeter is better than ± .5% and sensitivity is .002 J/mm. The vapour phase has been eliminated and the idea of thermally lagged multijacket has been achieved in practice.

INTRODUCTION

In modern experimental work on thermodynamic properties of mixtures, systems which show only small deviation from ideality and possess small heats of mixing are of great importance from the theoretical standpoint. In measuring small heats of mixing, the most important task is to eliminate errors due to evaporation. The recent work of McGlashan and Adcock (1954) seems to be the most successful effort so far in this line. Since then a few groups of workers are persuing this line but many systems could not be studied by this time, the need of which can not be over-stressed. In order to add more reliable data in this field a calorimeter has been constructed with certain important modifications to the MacGlashan-Adcock model to reduce the background fluctuation of temperature and uncertainty in the heat of stirring. The calorimeter is designed to use small quantities of liquids. It has been tested for a system for which standard data exist

DESCRIPTION OF THE CALORIMETER

Utilising the idea of Calvet (1945) and more recently by Tompa (1952) the troublesome vapour phase has been eliminated here by confining the liquid before and after the mixing under mercury The calorimeter shown in figure 1 consists of two unsilvered, double walled pyrex vessels each containing two bells. In the mixing vessel, the heat absorbed on mixing is compensated by an electrical heater, wound non-inductively on the outer bell, while the other vessel acts as a reference bath for the thermocouple. The concentric bells can be lowered or raised independent of each other, the inner one having a thin glass membrane at the top. The outer bell has a glass pointer projected inwards by means of which the membrane can be punctured Weighed amounts of liquids can be introduced, one into the inner bell and the other in the annular space

between the bells, by displacement of mercury. The reference vessel has exactly the same arrangement. By means of a mechanical coupling the outer and inner bells were connected in such a manner that this movement is simultaneous and identical in both the vessels. This is to eliminate the uncertainty due to

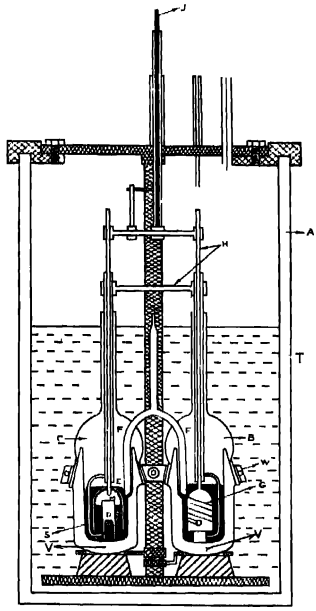

Fig. 1.

A—Lagged submarined jacket, B—Reaction vessel, C—Reference vessel, D—Inner bell, E—Outer bell, F—Ten junction thermocouple, G—Compensation heater, H—Mechanical coupler, J—Puncture rode, V—Outlet for evaporation, T—Outer thermostat.

heat produced by stirring. A ten-junction thermocouple with its ends insulated with "araldite" cement was used to measure the temperature difference. The jacket of the vessels can be connected to high vacuum line.

The calorimeter is mounted on a stout brass holder which can be suspended rigidly from a heavy brass lid of a thermally lagged jacket containing water. It is kept immersed under water in the water-tight jacket provided with outlets through which the mechanical coupler and electrical connections can be brought out. The thermally lagged jacket in its turn is kept submarined in a large thermostat fitted with a mercury-toluene regulator of 1.5 litre capacity and

efficient stirrers. The temperature of the outer bath is kept constant within $\pm$ 0.005°C.

The calorimeter is allowed to stand for 24 hours to attain equilibrium without any stirring inside the themally lagged jacket. This is done to achieve in practice the idea of themally lagged multi-jacket proposed by Tian (1922, 1923). Once the equilibrium is attained any fluctuation in the outer bath will have only a greatly reduced effect on the calorimeter itself due to thermal damping introduced by the lagged jacket. Thus an excellent reduction of background fluctuations of temperature can be achieved. Small temperature gradients may, however, be set up inside the thermally lagged jacket and this may vary slowly with time but the whole measurment lasts only for a short interval (not more than 10 mn) and as such, the gradients can be taken as permanent in nature during this interval. Also as the heat absorbed in the system is practically compensated and the mixer vessel is kept heavily damped by its highly evacuated wall during the experiment, the temporary small disturbance in the mixer vessel will practically have no effect on the permanent temperature gradients, if there be any. These gradients may cause only a small galvanometer deflection which remains fairly steady for short interval during the measurement. This can be taken as the zero of the galvanometer reading.

The jackets of the mixer and reference vessel are evacuated two hours before the measurements. Half an hour before the measurements, galvanometer deflections are observed at an interval of 10 mn. The membrane separating the two liquids is then punctured with a gentle push of the outer bell. Compensating current is switched on, for a predetermined period and the bells are raised up and down slowly to mix the two components properly. The galvanometer deflection after compensation is noted at definite intervals of time and a known amount of energy is again supplied to the system to account for the net uncompensated or over-compensated part

To check the uncertainty due to heat of stirring and heat produced due to puncture of the membrane, the bells in the mixer vessel is filled with the same component. The corresponding inside bell of the reference vessel is without any membrane. No measurable quantity of heat is found to develop for the the latter. As for the former, it is observed that if the stirring is very gentle and the quantity of mercury taken in both the vessels remains almost equal, then compensation due to heat of stirring is excellent and the galvanometer-zero remains completely unaffected by stirring.

Time intervals of compensating and calibrating currents are measured by means of a calibrated 50 cycle pulse generator and a scalar unit with a scale of ten. The output of the pulse generator is fed to the scalar unit via one pole of a D. P. D. T. switch. The other pole connects the heating circuit of the calorimeter to the storage cells. During the interval when current is sent to the

heating coil, the pulse generator is connected simultaneously to the scalar unit, from the count of which the time can be calculated with an accuracy of .02 seconds. The advantage of this type of arrangement lies in that it eliminates personal error without introducing any cumbersome mechanical systems like moving paper strips etc.

The electrical arrangement is similar to that of McGlashan and Adcock (1954) and the possible experimental errors have been fully discussed by them. Extending their estimate to that of our case, an accuracy better than $\pm$ 0.5% has been attained. The sensitivity of the calorimeter is approximately 002 Joules/mm.

EXPERIMENTAL

In order to test the calorimeter the heat of mixing of the system carbon tetrachloride and cyclohexane was studied at 40 0°C for which reliable data exist.

Analar carbon tetrachloride was refluxed at 50°–60°C with an alcoholic solution of potassium hydroxide (1 · 1 by weight). The alcohol was then removed by shaking with water followed by shaking with small portions of concentrated sulphuric acid, until there was no colour. It was then first distilled in an all glass assembly and finally fractionated through a column of 40 theoretical plates Only the middle fraction was collected The purity of the sample was checked by measuring the density. At 25°C the density of the sample was found to be 1.58423 gm/cc which possibly can be compared to 1.5858 gm/cc obtained by McGlashan *et al.* (1954) and 1.58452 gm/cc by Scatchard at the same temperature

RESULTS

TABLE I

At temperature 40°C

Wt. of carbon tetrachloride	Wt. of cyclo-hexane	mole fraction of CCl_4 in mixture	h in J	H_m in J/mole
1 5829	8261	.488	2.85	141.9
2 0576	.5512	.329	2.46	124.7
2.3748	.3937	.233	2.03	100.7
2.6909	.2361	138	1.35	66 5
1.1077	1.0228	.628	2.53	130.8
.7922	1.0808	.731	2.09	109.2
4751	1.3382	837	1.45	76 1

Analar cyclohexane was washed several times with a cold mixture of concentrated sulphuric and nitric acids to nitrate any benzene that might have been

present. After repeated washings with distilled water it was dried and distilled over metallic sodium. Finally it was fractionated through a column of 40 theoretical plates. The density of the sample measured at 25°C was 0.77395 gm/cc while those obtained by McGlashan *et al.* (1954) and Scatchard at 25°C is 0.77375 gm/cc and 0.77383 gm/cc respectively.

The results of our work and that of McGlashan *et al.* have been plotted on the same graph in figure 2. The agreement is found to be quite satisfactory.

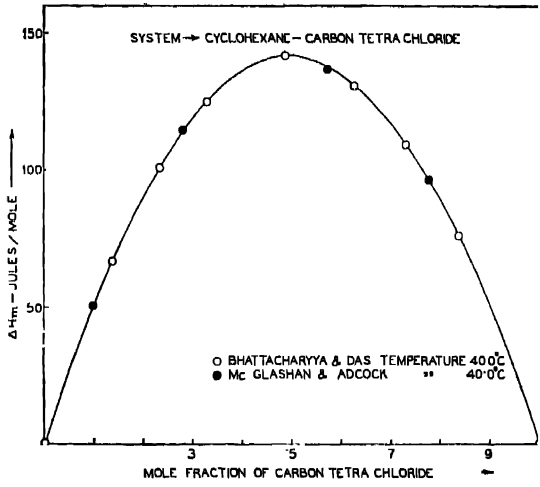

Fig. 2

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